

# UNITED STATES PATENT OFFICE

2,461,478

## GELATIN SUBBING COMPOSITIONS HAVING ANTISTATIC PROPERTIES

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7 Claims. (Cl. 106—135)

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This invention relates to photographic film, and more particularly to gelatin subbing compositions having anti-static properties.

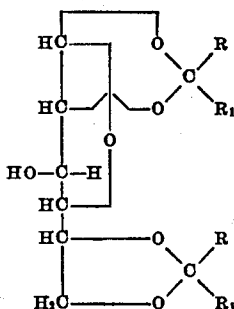
Considerable difficulty has been encountered in the manufacture of photographic film due to the accumulation of electrical charges on the film. In one step of the manufacture of photographic film, a film base is coated on one or both sides with a subbing composition which usually consists of a dispersion of gelatin in a suitable solvent or solvent mixture, so as to facilitate the adherence, or anchorage, of one or more of the photo-sensitive, non-curling, or anti-halation layers. When such a laminate is wound into a tight roll and subsequently unwound, as during a coating operation, considerable static electricity is generated and spark discharges readily occur. Manifestations of these charges are glow discharges which after development of the coated and exposed film show up as black streaks or lines, or as irregular fogged patterns in the emulsion layer. Attempts have been made to overcome static in such laminates by the incorporation of substances into subbing compositions which are electrolytes or possess hygroscopic properties. The function of these substances is to impart conductivity to the film and thus dissipate the charges before their accumulation leads to local discharges. Many of these substances are incompatible with gelatin subbing compositions and introduce new manufacturing difficulties.

An object of the present invention is to provide gelatin subbing compositions having anti-static properties.

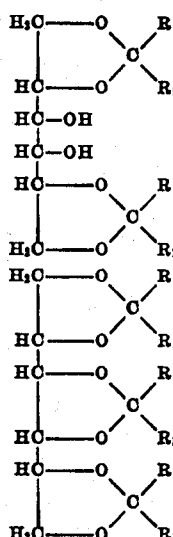
A further object is to provide gelatin subbing compositions which reduce static charges on a photographic film base during coating of the sensitive silver-halide emulsion, non-curl, or anti-halation layers.

Further objects will appear hereinafter.

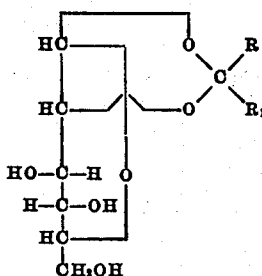
These objects are accomplished by the present invention by incorporating, into any gelatin subbing composition, a compound of the group consisting of acetals and ketals of hexoses and hexitols, of the following general formulae:



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and



wherein R is either hydrogen or an alkyl group of not more than 2 carbon atoms and R<sub>1</sub> is an alkyl group of not more than 3 carbon atoms, R always being hydrogen when the compounds are acetals.

As suitable examples of such acetals and ketals, the following may be mentioned:

- Di-acetone hexitol
- 45 Di-acetone glucose [di(isopropylidene) glucose]
- Di-isobutylidene glucose
- Di-(n-butylidene)-mannitol
- Di-propylidene glucose
- 1,2-mono-acetone glucose
- 50 1,2-mono-propylidene glucose
- Tri-acetone hexitol
- Tri-(n-butylidene)-glucose
- Tri-(n-butylidene)-mannitol

55 These acetals and ketals are incorporated into any gelatin subbing composition containing gelatin, water dispersing medium, such as an organic acid, i. e., acetic acid, and the like, and an organic solvent or a mixture of such solvents. The amount of these acetals and ketals, which may be employed as an anti-static medium, may range

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3 from about 0.5% to 10%, and preferably from 1% to 3%. The gelatin may range from about 0.5% to 1.5%, preferably from about 0.75% to 1.0%, the balance being water, gelatin dispersing medium, and an organic solvent or mixture of such solvents. All proportions are by weight.

The anti-static gelatin subbing compositions are prepared by adding the acetals and ketals to a gelatin dispersion containing gelatin, water, and a dispersing medium, and thereafter adding the dispersion to an organic solvent or mixture of such solvents, or by adding the acetals and ketals to the finished gelatin subbing composition, i. e., containing the organic solvent or mixture thereof. Slight warming and agitation will facilitate the dissolution of the acetal and ketal.

The solution thus obtained is deposited on one or both sides of a film base in any convenient manner, the subbing operation preferably being carried out in connection with, or as a part of, the process of making the film support itself. The gelatin subbing solutions made up as above described are clear dispersions.

The film bases used in accordance with this invention are the cellulose derivatives, e. g., cellulose nitrate, cellulose acetate, and other lower fatty acid esters of cellulose including simple and mixed esters, such as cellulose propionate, cellulose butyrate, cellulose acetate-propionate, cellulose acetate-butyrate, and the like, ethers of cellulose, such as the ethyl ether, benzyl ether, and the like, and the fusible, water-insoluble, synthetic linear superpolymers used for film elements as described in United States Patents 2,071,250, 2,071,252, 2,071,253 and 2,130,948.

It will be appreciated that each different type of cellulose ester, ether, and mixtures thereof, including the synthetic linear superpolymers, requires a slightly different solvent or solvent combination. The solvent or solvent mixture employed must be such that it will have a solvent or at least a softening or swelling action on the film base so as to stick or anchor the gelatin upon the area of the support which has been softened or swollen. For example, with a cellulose acetate base a low molecular weight alcohol, e. g., methanol, ethanol, and the like, or a ketone, such as acetone or a mixture of 3 parts alcohol to one part of acetone may be employed. With cellulose acetate-propionate film base, an alkyl ester, such as, for example, methyl acetate, ethyl acetate, butyl acetate, and the like, either alone or with methanol or 1,4-dioxane may be effectively employed. For the superpolymers there may be used mixtures of low molecular weight alcohols, such as methanol, ethanol, and the like, with phenols and salicylic acid. It may be pointed out at this point that the nature of the gelatin dispersing medium, solvent, or solvent mixture is immaterial so long as the dispersing medium, whether it be an organic acid, heterocyclic nitrogenous base, lactone, or the like, disperses the gelatin in water, and the solvent or solvent mixture wets or bites into the cellulose derivative or other materials employed as a film base. The term "gelatin dispersed in a solvent for said support" as used in the claims should be construed to embrace these dispersing mediums and solvent or solvent mixture. Since the materials suitable for film base and their solvent properties are known, no difficulty is presented in selecting a suitable solvent or solvent mixture for use in the subbing compositions.

The following specific examples illustrate several of the various methods of applying these

4 acetals and ketals as anti-static agents in gelatin subbing compositions, and it will be understood that these examples merely represent the preferred embodiments and are not to be considered as limitative.

#### Example I

A film base of cellulose acetate was coated with the following gelatinous substrating composition:

	Parts
10 Gelatin -----	0.73
Water -----	1.33
Acetic acid -----	1.20
Di-acetone glucose -----	1.34
15 Methanol -----	75.53
Acetone -----	19.87

After the subbing layer had dried, the usual light-sensitive emulsion layer was coated directly thereon. During the coating of the light-sensitive emulsion upon the subbed base no static electricity was generated. After exposure and processing the emulsion adhered tenaciously to the cellulose acetate film support, and the developed film showed no black streaks or lines.

#### Example II

A film base of cellulose acetate-propionate having an acetyl content of 30% was coated with the following subbing composition:

	Parts
30 Gelatin -----	1.0
Water -----	2.5
Acetic acid -----	1.5
35 Di-acetone hexitol -----	1.0
Methanol -----	74.0
Methyl acetate -----	20.0

After the subbing layer had dried, the usual light-sensitive emulsion layer was coated directly thereon. During the coating of the light-sensitive emulsion upon the subbed base no static electricity was generated. After exposure and processing the emulsion adhered tenaciously to the cellulose acetate film support, and the developed film showed no black streaks or lines.

#### Example III

A film base prepared from poly (vinyl chloride-vinyl acetate) was coated with the following subbing composition:

	Parts
50 Gelatin -----	0.5
Water -----	2.5
55 Acetic acid -----	1.5
Tri-acetone hexitol -----	1.5
Methanol -----	32.0
Acetone -----	62.0

After the subbing layer had dried, the usual light-sensitive emulsion layer was coated directly thereon. During the coating of the light-sensitive emulsion upon the subbed base no static electricity was generated. After exposure and processing the emulsion adhered tenaciously to the cellulose acetate film support, and the developed film showed no black streaks or lines.

#### Example IV

	Parts
70 Gelatin -----	1.5
Water -----	15.0
Salicylic acid -----	0.5
Diamyl phenol -----	3.5
1,2-mono-acetone glucose -----	1.5
75 Methanol -----	78.0

The foregoing composition was found to be excellent as a sub for a synthetic linear polymer film base of the type described in United States Patents 2,071,250, 2,071,252, 2,071,253 and 2,230,948.

The subbed photographic film bases produced according to the present invention, in addition to preventing the accumulation of static electricity when unwound during a coating operation, were found to be very satisfactory from the standpoint of physical requirements, such as, high strength, flexibility, and good water-resistance.

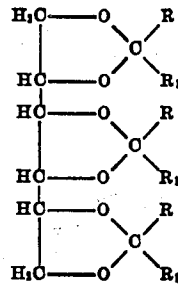
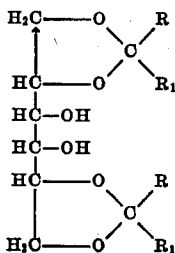
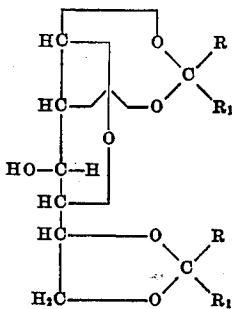
The small quantity of the acetal or ketal, which may remain with the gelatin after evaporation of the water and organic solvent from the subbing composition, has no adverse effect upon the light-sensitive emulsion layer, nor has the subbing composition any adverse effect upon the containers in which it is stored, or upon the coating equipment employed.

It will be understood that wherein the claims appended hereto the term "subbing" is used, that such is intended to include the operation of applying a subbing layer from any one of the subbing compositions prepared in accordance with the present invention.

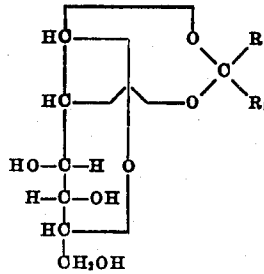
While the present invention has been described in considerable detail with respect to certain preferred materials, it is understood that the class of gelatin dispersing agents, solvents, or mixture of such solvents is not limited thereto and that numerous variations and modifications described in the foregoing specification may be made. As for example, a mixture of two or more of the acetals and/or ketals may be employed as anti-static agents. Similarly, a film support may be coated on both sides with the subbing compositions prepared in accordance with the present invention for the preparation of X-ray film, wherein both subbed sides are coated with a suitable gelatino silver-halide emulsion.

I claim:

1. An anti-static gelatin composition suitable for the subbing of a photographic film support, which comprises a gelatin subbing composition containing a member of the group consisting of ketals and acetals of hexoses and hexitols of the following general formulae:



and



wherein R is a member selected from the class consisting of hydrogen and an alkyl group of 1 to 2 carbon atoms, and R<sub>1</sub> is an alkyl group of 1 to 3 carbon atoms.

2. An anti-static gelatin composition suitable for the subbing of a photographic film support, which comprises a gelatin subbing composition containing from 0.5 to 1.5% of gelatin, from 1.33 to 15% of water, from 78 to 95.4% of a solvent for said support, and from 0.5 to 10% of di-acetone glucose.

3. An anti-static gelatin composition suitable for the subbing of a photographic film support, which comprises a gelatin subbing composition containing from 0.5 to 1.5% of gelatin, from 1.33 to 15% of water, from 78 to 95.4% of a solvent for said support, and from 0.5 to 10% of di-acetone hexitol.

4. An anti-static gelatin composition suitable for the subbing of a photographic film support, which comprises a gelatin subbing composition containing from 0.5 to 1.5% of gelatin, from 1.33 to 15% of water, from 78 to 95.4% of a solvent for said support, and from 0.5 to 10% of tri-acetone hexitol.

5. An anti-static gelatin composition suitable for the subbing of a photographic support which consists of the following constituents:

	Parts by weight
55 Gelatin	0.73
Water	1.33
Acetic acid	1.20
Di-acetone glucose	1.34
60 Methanol	75.53
Acetone	19.87

6. An anti-static gelatin composition suitable for the subbing of a photographic support which consists of the following constituents:

	Parts by weight
70 Gelatin	1.0
Water	2.5
Acetic acid	1.5
Di-acetone hexitol	1.0
Methanol	74.0
Methyl acetate	20.0

75 7. An anti-static gelatin composition suitable

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for the subbing of a photographic support which consists of the following constituents:

	Parts by weight	
Gelatin -----	0.5	
Water -----	2.5	5
Acetic acid -----	1.5	
Tri-acetone hexitol -----	1.5	
Methanol -----	32.0	
Acetone -----	62.0	

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REFERENCES CITED

The following references are of record in the file of this patent:

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Number	Name	Date
2,313,570	Nadeau et al. -----	Mar. 9, 1943
2,341,887	Middleton et al. ----	Feb. 15, 1944